

**Environmental Impact Assessment: Looking at Sediments in Nootka Sound for
Traces of Pulp Mill Effluent**

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5-31-2015

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Acknowledgments

I would like to thank Julian Sachs for the guidance, advice, and encouragement he gave me throughout this difficult project. Thank you Arthur Nowell for taking the time throughout the year to listen to my progress, offer advice, and words of wisdom. I am tremendously grateful for Ashley Maloney and Josh Gregersen who always took time out of their day to help me in lab. Thank you to my fellow students who have helped me throughout this project including Julia Marks and Trevor Harrison. I would also like to thank the crew of the *R/V Thompson* for their help in a very hectic cruise, and always providing advice and assistance. Lastly, I would like to thank the University of Washington School of Oceanography for financing this class and making this incredible experience possible.

Abstract

The production of pulp, a paper product, involves a combination of chemical washes and combustion processes that are known sources of many persistent organic pollutants that can bio-accumulate in the environment with deadly effects. This paper investigates sediments collected from Nootka Sound, BC for traces of pulp mill effluent, specifically 2,3,7,8 tetrachlorodibenzo-p-dioxin and 2,3,7,8 tetrachlorodibenzofuran, potentially deposited there from a pulp mill that operated in the area from 1964-1998. 1.305ng/g of dioxins were detected at one depth in sediment that likely settled in 1988. Despite the positive detection of dioxins during a time the mill was in operation, further sediment analysis was not possible due to a high quantity of hydrocarbons, that restricted the remaining samples from complete analysis. Further investigation into these sediments requires a more reliable method to consistently analyze samples, but is warranted by the alarming amounts detected.

Introduction

Pulp is a wood product that is a component in the production of paper. A particular type of mill, known as a kraft mill, uses chlorine bleaching compounds like chlorine dioxide and hydrogen peroxide (Ali and Sreekrishnan 2001) to further change the color of pulp to the desired color. These mills are typically located next to large bodies of water due to the amount required for the pulping process and as a result, effluent containing harmful contaminants is often drained into the same body of water as means to remove waste from the plant. The mixture of pollutants emitted from the plant contains several that resist degradation and persist in the environment. These chemicals include resin acids, sulfur compounds, phenols, and most notably dibenzodioxins and dibenzofurans. Some studies have shown that most of these chemicals are recalcitrant to degradation via microflora in the surface waters (Ettinger and Ruchhoft 1950) and aerobic and anaerobic bacteria (Ali and Sreekrishnan 2001). However, dibenzodioxins and dibenzofurans are considered by the EPA as probable human carcinogens (USEPA 1999) and are considered persistent organic pollutants that have half-lives in soil up to fifty years (EPA Dioxin fact sheet). These pollutants have been shown to attach to suspended sediments and get transported downstream of the mill site where they potentially can accumulate in benthic crabs (Yunker and Cretney 1996), fish (Owens et al 1994, Amendola et al. 1989), and sediment (Kim Oanh et al. 1995).

In 1964 a kraft bleach pulp mill was built in Nootka Sound, a small fjord estuary on the west side of Vancouver Island, at the mouth of the Gold River. The

river feeds directly into Muchalat Inlet, one of the three major Inlets in the Sound. The pulp mill operated until changing market demands forced the mill to close in 1998. However before its closure a series of regulations called the Pulp and Paper Mill Effluent Chlorinated Dioxins and Furans Regulations went into effect July 1, 1992. These regulations prohibited the release of 2,3,7,8 tetrachlorodibenzo-p-dioxin (2,3,7,8 TCDD) and 2,3,7,8 tetrachlorodibenzofuran (2,3,7,8 TCDF), two of the most toxic dioxin and furan congeners, in final pulp mill effluents. Although the mill closed shortly after the start of these regulations, there is roughly a twenty five year period in which unregulated mill effluents were released into the Muchalat Inlet. This poses the major question of how may have this impacted the environment, specifically Muchalat Inlet?

Previous literature has shown a spatial gradient of TCDD/F's leading away from kraft mill pulp sites in both sediment and biota samples (Koh et al. 2004)(Owens et al. 1994). Similarly, a pulp mill in Vietnam was studied to quantify the accumulation of dioxins in the environment and found traces of 2,3,7,8-TCDD/F in the sediment of the river receiving the effluent, in the sediment of a nearby fish pond, and within the fish themselves (Kim Oanh et al. 1995). There are no similar impact studies looking at dioxins on the Gold River pulp mill. However, a series of environmental impact assessment measurements were performed shortly before the mill opened and continued for several years after to monitor the effects of the mill and ensure effluent discharges were within permit limits. Although these reports did not test for dioxins and furans, they reveal that on average for the year 1976 and 1977 the effluent discharge contained approximately 1100 and 900

pounds of suspended solids, respectively, per day into Muchalat Inlet (Sullivan and Nelson 1979).

Given dioxins attach to suspended particles and the mill operated in a time period where the environmental impacts of mill effluent were not fully understood, I hypothesized that the sediment proximate to the mill will have detectable levels of 2,3,7,8-TCDD/F's, and furthermore, that these contaminants will be present in concentrations that pose a high risk to aquatic and mammalian wildlife as defined by the EPA (USEPA 1993). An environmental impact assessment like this could provide insight to the effects of a single pulp mill almost two decades after its closure. So far, I have been unable to find a similar study determining effluent impacts from a closed mill. This information could be applied to current pulp mill operations around the world, especially those in developing countries where advanced and "cleaner" techniques are often substituted for older technologies borrowed from developed countries (Kim Oanh et al. 1995).

Methods

Location

Sediment samples were collected aboard the *R/V Thompson* from Muchalat Inlet in Nootka Sound, BC (Fig. 1). Station M04a (49° 40'03.8" N 126° 09'46.5" W) was selected for its proximity to the pulp mill, approximately 348 meters deep and 2500 meters west of the effluent discharge pipe. Further west is station M06a (49°

39°55.2' N 126° 10'47.4' W), approximately 350 meters deep and 3700 meters west of the effluent discharge site. Sediment cores were collected in December of 2014.

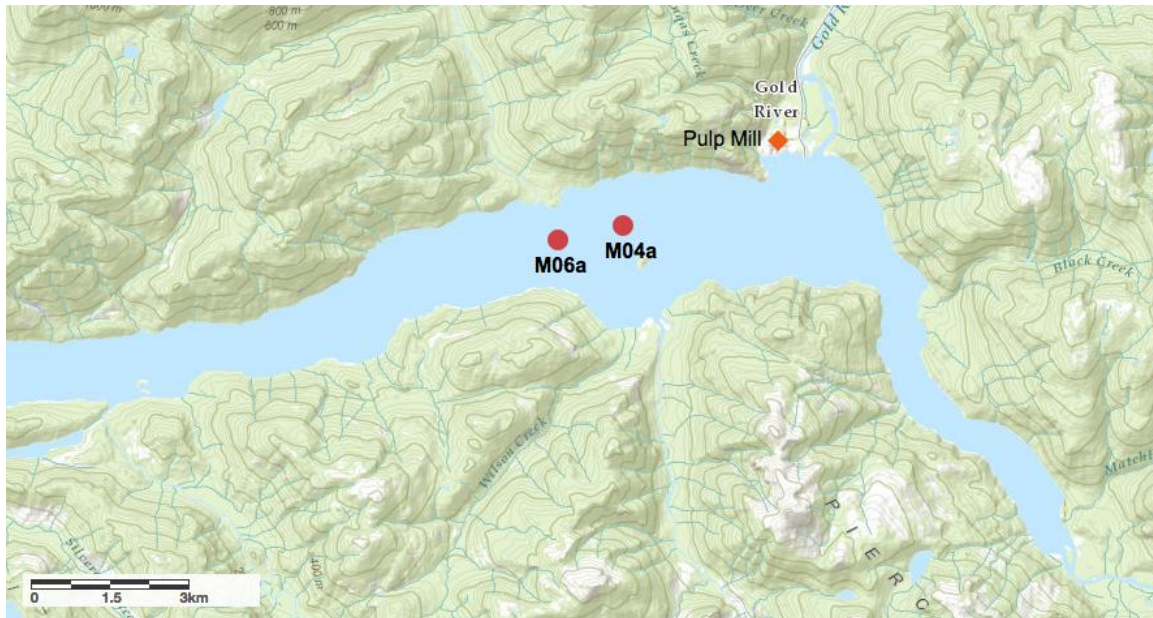


Figure 1. Map of Muchalat Inlet in Nootka Sound, BC. Stations are indicated by the red dots while the location of the pulp mill is indicated by the orange diamond.

Sediment Collection

Sediment samples were collected using a spade box corer with a modified base to avoid over penetrating into the sediments and losing the surface layers. A box core was taken at the M04a and M06a station. The box used for containing the sediment was approximately 60cm tall. Once removed from the corer, the box was subsampled with a 6 inch diameter PVC tube and a sediment X-ray tray, both 60cm tall. The sediment from the 6 inch PVC tubes was then extruded in 1cm increments for the top 10cm, and 2cm increments until the bottom of the core, and stored in labeled whirlpak bags. Additionally, a modified kasten core (approximately 187cm in length) was taken at the M04a station. Sediment was subsampled with X-ray trays

(30cm in length) along the length of the core. The sediment was then segmented using thin metal plates inserted at 1cm increments for the top 30cm, then segmented at 2cm intervals. Segments were scooped out using metal spatulas and bagged in labeled whirlpak bags. Sediment samples were kept refrigerated at 4 °C and in the dark until analysis.

Sediment tray imaging

X-ray trays were scanned using a Siemens biograph 16 CT scanner at Via Radiology in Seattle, WA. Images shown were selected for minimal void spaces resulting from the sediment drying out.

Radiocarbon dating

Organic material was collected at depths of 12-14cm, and 18-20cm from the box core at M04a station, and at depths of 40-41cm, 45-46cm, and 50-51cm from the kasten core from the M04a station. Sediment was placed onto size 0 and -1 phi sized screens and flushed with water to remove fine-grained sediment and retain macrofossils. Pieces of leaves or needles from trees were selected over wood and bark because wood material can be decades to centuries older than co-deposited leaves. Terrestrial macrofossils were then stripped of extrinsic organic material with repeated rinses in weak acids and bases. First they were submerged in hydrochloric acid, HCl, and set in an oven at 80°F for 20 minutes. The HCl was then

pipetted off, and samples were rinsed in water five times, before being submerged in sodium hydroxide, NaOH, and placed back in the oven for 20 minutes. The NaOH was pipetted off and rinsed with water five times, before being submerged in HCl and put back into the oven for 20 minutes. The HCl was pipetted off and the samples were rinsed with water five times, then placed back in the oven overnight to dry all excess water. Samples were weighed and shipped for analysis. DirectAMS in Bothell, WA performed radiocarbon analysis. Radiocarbon concentrations were converted to calendar years using software at <http://calib.qub.ac.uk/CALIBomb/>.

Sample Extraction

2,3,7,8 TCDD/F extraction from the sediment was performed using the Dionex ASE 200 accelerated solvent extractor in the method described by McCant et al. (1999). The method was tested by putting known quantities of both TCDD analytical standard (Sigma Aldrich, 48599) and TCDF analytical standard (AccuStandard, APP-9-170) into a blank ASE cell and testing for percent recovery. At least 50 grams of dried sediment per depth was extracted to ensure the detection of dioxins and/or furans. The extract, in the form a solution, was flushed with water and pipetted into a separate container. The pH of the water was tested for acidity, to ensure the extract solution was not acidic before being injected onto the gas chromatograph and mass spectrometer (GC/MS). Samples were then dried down using compressed nitrogen gas and stored in combusted 33ml vials.

Sample Cleanup

To remove the high concentrations of elemental sulfur dissolved within the extract, the solution was passed over an activated copper column. The copper columns were made by placing a small amount of combusted glass wool into combusted glass Pasteur pipettes, and compacting the wool at the bottom near the tip to act as a filter. Combusted sand was placed on top of the wool, followed by copper filings. The amount of copper filings varied based on the amount of sulfur present. The column was then activated with 6N HCl. HCl was added until all the copper was visually activated (indicated by the copper turning pink). The column was then flushed with water, and the pH of the water was measured as it left the column until it was pH neutral. Excess water was removed by flushing the column with methanol (MeOH). To remove excess methanol the column was then flushed with dichloromethane (DCM). The dried samples were then brought up in DCM, using a vortex shaker and sonicator to dissolve the entire sample, which was transferred to the activated copper column. The copper was observed to turn from pink to black as it reacted with the sulfur forming copper sulfide. If the entire column turned black the sample was passed through a second copper column. Once the column is no longer turning fully black, the sample was dried down using nitrogen gas and stored in combusted 11ml vials.

Sample Analysis

The dried samples were dissolved in DCM and transferred into 250 μ L glass inserts inside 2mL glass GC vials, and dried down. When the samples were ready for analysis, they were brought up to a volume of 10 microliters in toluene. The Agilent 6890N GC system and Agilent 5975 mass spectrometer were used for TCDD/F quantification. The GC was equipped with an Agilent VF-17 GC column (60 m x 320 μ m x 0.25 μ m). The oven temperature began at 110 °C and increased to 320 °C at 4°C/min. The ion source temperature in the mass spectrometer was 220°C and the ionization energy was 70 eV. A series of calibration standards, of concentrations 5, 10, 15, 20, and 25 nanograms/microliter, were prepared to derive a calibration curve that the sediment extract samples could be compared to (Fig. 2). In order to maximize the sensitivity of the analysis the GC/MS was run in select ion monitoring mode, or SIM mode, selecting ions with specific mass to charge (m/z) values of the 2,3,7,8 TCDD (322 and 320 m/z) and TCDF (306 and 304 m/z) ions.

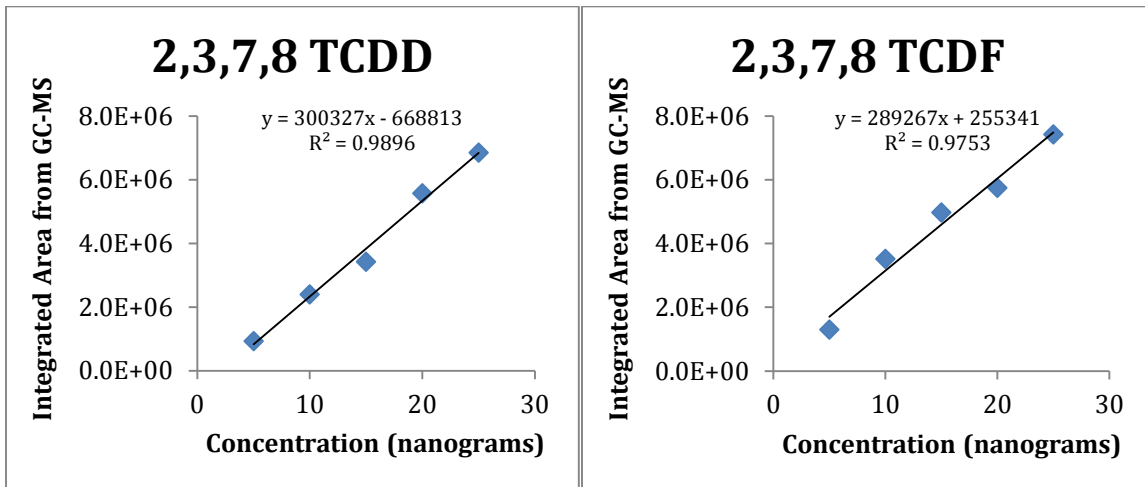


Figure 2. Calibration curve used to quantify TCDD/F detections on the GC/MS.

Results

Radiocarbon dates estimated from the M04a box and kasten cores were plotted together (Fig. 3). The two dates collected from the box core at depths 13cm and 19cm, 1987 and 1975 respectively, result in a sedimentation rate to be approximately 5mm year⁻¹. The three dates collected from the kasten core at 30cm (1978), 40cm (1959), and 45cm (1963) were plotted with an additional surface control point (0cm, 2015) and resulted in a sedimentation rate to be approximately 7.79mm year⁻¹.

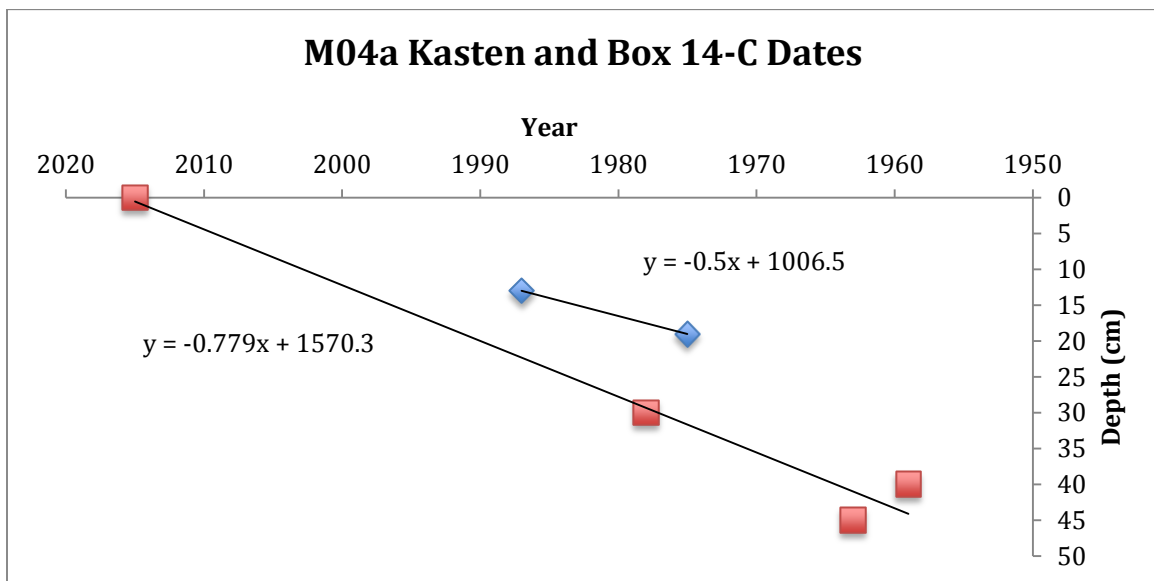


Figure 3. Combined radiocarbon dates from both the M04a box (blue) and kasten (red) cores. Estimated sedimentation rates come from the slope of the linear regressions.

Analytical external standards of 2,3,7,8 TCDD/F that were injected into sediment and run through the entire extraction and cleanup process showed a 93.2% recovery for TCDD and a 75.5% recovery for TCDF. Additionally, these standards showed a retention time of approximately 36 minutes.

No traces of TCDF were detected at the observed depths at station M04a

(Table 1). At a depth of 10-12cm, TCDD was found in a concentration of 1.305ng /g

(Fig. 4 and 5). TCDD was not detected at any of the other depths.

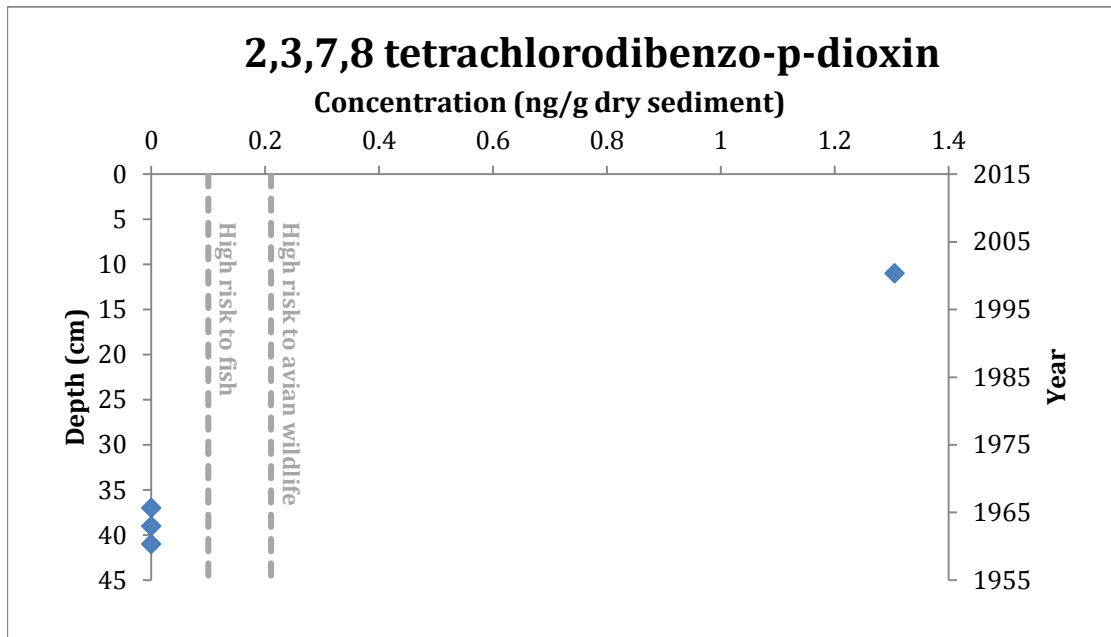


Figure 4. Plot showing the down-core concentrations of 2,3,7,8 TCDD at the M04a station. Concentrations are given as nanograms of TCDD per dry gram of sediment, plotted against the depth at which they were found (cm) and at what year the sediment was likely deposited at given a sedimentation rate of 7.79mm year⁻¹. Grey dashed lines represent the minimum high-risk concentration for TCDD in sediment in relation to fish and avian wildlife (US EPA 1993).

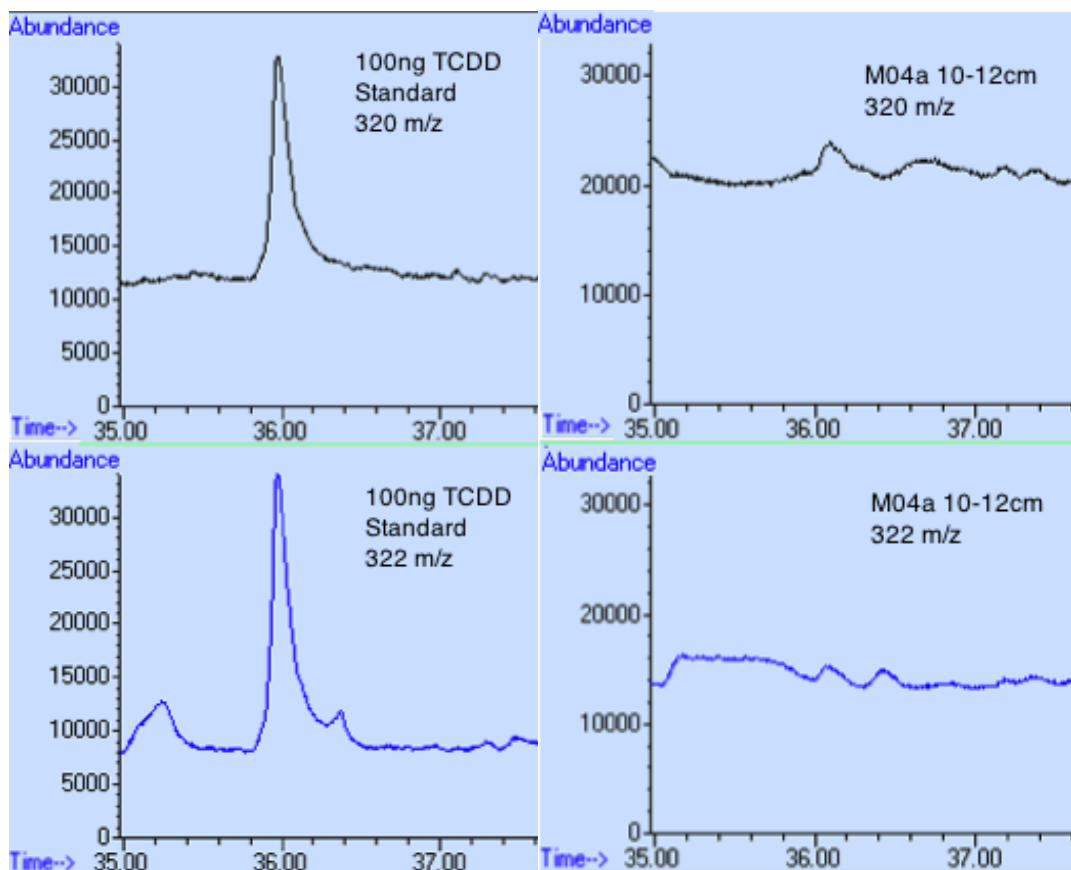


Figure 5. Chromatograms for 100ng of TCDD analytical standard (left) and the detected TCDD concentrations found at M04a 10-12cm (right). Chromatograms for ions with a m/z of 320 are shown in black, and ions with a m/z of 322 are shown in blue.

Table 1. List of all the depths analyzed for TCDD/F and their respective station. Samples that could not be fully analyzed due to hydrocarbon contamination are marked as (-).

Station	Depth (cm)	Concentration (ng/g dry sediment)	
		TCDD	TCDF
M04a	6-8	-	-
M04a	10-12	1.305	0
M04a	14-16	-	-
M04a	20-22	-	-
M04a	36-38	0	0
M04a	38-40	0	0
M04a	40-42	0	0
M06a	14-16	-	-
M06a	20-22	-	-

Discussion

The collected sediment from Muchalat Inlet is more difficult to assess for TCDD/F than previously expected due to the many additional substances they contain. However, the laminated sediments found in Muchalat Inlet make it an ideal test location for this type of study, and make it possible for coupling effluent concentrations to a specific date in time.

First the generated age model and sedimentation rate will be discussed in detail including possible errors in the model itself and the effectiveness of using radiocarbon dating. Next the presence and location of TCDD/F, if any, will be addressed. Finally the effectiveness of the extraction and quantification method will be discussed, as well as its outlook for use in future studies.

Age Model

There are many different ways to interpret the estimated age model generated from the box and kasten cores. Although the separate cores spatially do not line up and generated slightly different sedimentation rates, the data from the box core is likely to be more inaccurate due to errors made during sampling. Upon recovering the box core from deployment it was clear that it had over penetrated into the sediment and is very likely that the sediment at the top of the box was not representative of the surface. Additionally, because the boxes over penetrated and were completely filled, more of the top sediment was removed to allow space for the

expanding plug used to seal off the top of the 6 inch PVC tubes. The kasten core, however, showed no apparent signs of over penetration. Because the kasten core appeared to have recovered the surface sediments, a surface control point was added to the kasten data in Figure 3, and used for the linear regression. The combination of factors that resulted in a loss of surface sediment could explain why the two radiocarbon dates from the box core appear approximately 10cm shallower compared to the kasten core, and still yield relatively similar sedimentation rate. However, because the kasten core did not over penetrate and has a usable surface control, the best estimation of an age model should use the 7.79mm year^{-1} sedimentation rate.

Although radiocarbon dating is a useful alternative compared to other dating techniques for recent sediment, e.g. lead-210, the inaccuracies that are associated with it make calculating an age model difficult when using a limited number of samples. This is largely due to the fact that when using the “bomb calibration curve” a single radiocarbon value will not result in just one date, but instead the probabilities of multiple dates, making selection of a date difficult at times (Fig. 6). There is also no way of determining whether a macrofossil is representative of the time it was deposited, as it could have been deposited on land for some years before being transported to the sea and deposited in sediment. Ideally, more accurate age models could be generated by first sending out a few samples to approximate dates within the core, then heavily sampling and analyzing specific areas. Additionally, if funds for radiocarbon dating are limited, samples should be focused in a single core.

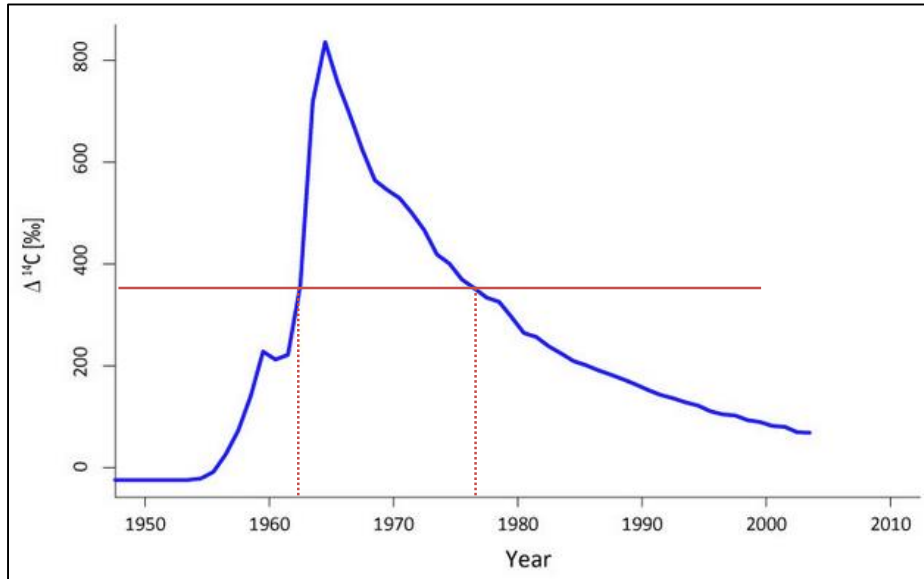


Figure 6. Bomb calibration curve (blue) showing the past atmospheric radiocarbon levels. Red lines are used to show that a single radiocarbon value can result in multiple dates.

Dioxin and Furan Concentrations

TCDD was detected at only one depth, 10-12cm, which corresponds to the calendar year 2000 according to our best estimate of age. Although the year 2000 is well after the closing of the pulp mill, the measured depths of sediment taken from the box core is likely off by approximately 10cm, as discussed earlier. Assuming an offset of 10 cm would result in TCDD really being detected at a depth of 20-22cm, which corresponds to the year 1988. A concentration of 1.305ng/g dry sediment well exceeds the minimum high-risk concentration in sediment for fish (0.1 ng/g), mammalian wildlife (0.025 ng/g), and avian wildlife (0.21 ng/g) as defined by the EPA (EPA 1993). While this is an alarmingly high concentration it comes from an undisturbed portion of the sediment core (Fig. 7). The extent of these laminated sediments show a lack of activity from borrowing organisms in this area for several

decades. Because of this, there appears to be little to no threat of the TCDD being cycled to the surface sediments. Four other depths (36-38cm, 38-40cm, and 40-42cm) that were sampled contained no detectable TCDD or TCDF concentrations. This is slightly surprising as the shallowest of those depths (36-38cm) corresponds to a calendar date of approximately 1967, a time where the mill would have been in operation for three years. This could be a result of reduced pulp production during the early stages of the plants operation. Increased production years later could have deposited larger quantities of TCDD/F that are detectable using this method. A more likely explanation is a slight inaccuracy in the age model. A sedimentation rate slightly less than 7.79mm year^{-1} , like the rate generated from the box core, would put the 36-38cm depth at an earlier period in time. To supplement the one detection of TCDD, five other samples from varying depths were prepared for GC/MS analysis. However, they could not be fully processed due to a mysterious oil that could not be removed, as discussed below.

No traces of TCDF were detected. Although studies have shown TCDFs to be less recalcitrant in sediments compared to TCDDs, approximately 60 years and 90 years respectively, it is unlikely to be the determining factor (Kjeller and Rappe 1995). Other possible explanations could be a difference in the bleaching process from other pulp mills, resulting in a different and unique dioxin and furan congener profile compared to other mills.

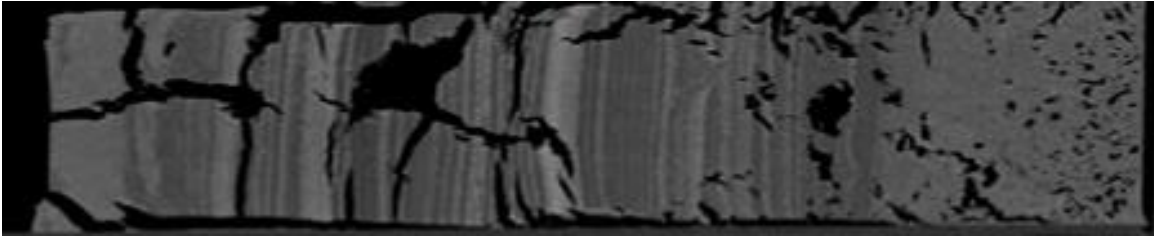


Figure 7. CT scan of the M04a box core sediment tray. Starting with the top of the core (left) to the bottom (right), the tray is approximately 60cm long. The black spaces of voids in the sediment caused by drying of the tray.

Effectiveness of method for TCDD/F assessment in sediments

Although the extraction method described by McCant et al. (1999) was reported to be capable of producing an extract that required no cleanup procedures, our experience was that an additional cleanup processes had to be added along the way. Additionally our second batch of samples was plagued by an unidentified source of hydrocarbons (Fig. 8).

The first problem that was encountered with this method was the presence of large amounts of sulfur. Initially this was discovered when the extract was dried, causing sulfur to precipitate out of solution. Although not expected, this issue was relatively easy to circumvent through the use of acid activated copper columns. Given that the high recovery percentage of the recovery standards, it is unlikely that these copper columns affected the TCDD/F concentrations within the sample.

A major problem that remains unsolved for this method was the presence of an oil that could not be evaporated and was present in high enough quantities that it could not be directly injected onto the GC in fear of ruining the column. Using the GC/MS, a diluted sample of the oil was tested using SCAN mode, different from SIM

mode in that it detects all ions, and was found to be various hydrocarbons most closely resembling alkene chains (Fig. 8).

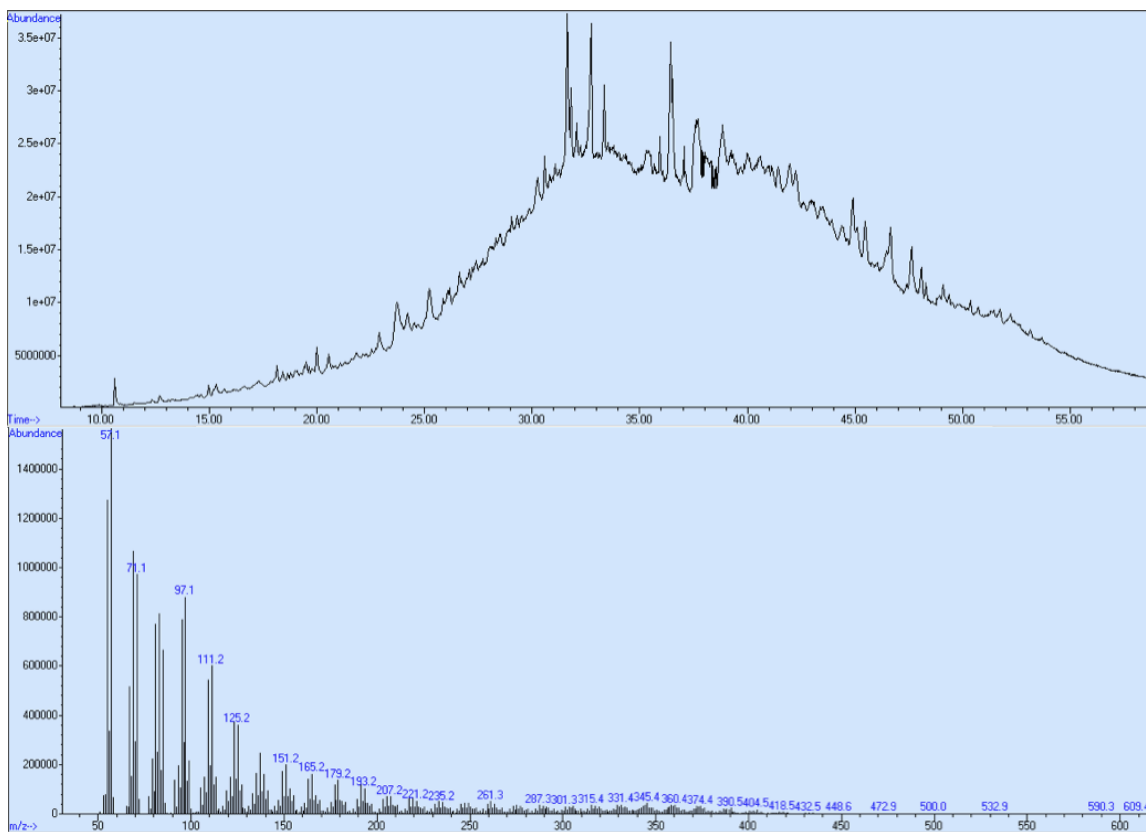


Figure 8. Total ion chromatogram, or TIC, (top) and mass spectrum (bottom) of the hydrocarbon contamination. Mass spectrum taken from the middle of TIC at approximately 35 minutes.

Silica gel columns were used in an attempt to separate the hydrocarbons from any traces of TCDD/F, using the method described by Nelson and Sachs (2014). This method was initially applied to a known amount of TCDF analytical standard to observe in which of the four silica gel fractionations the solution was eluted. GC/MS results showed that the analytical standard did not entirely elute in the second fraction, as predicted, rather was spread across both the first and second with the majority in the first fraction. The test was repeated modifying the method using completely activated, as opposed to 5% deactivated, silica gel, and yielded

similar results. Lastly, this method was applied to a diluted fraction of a sample contaminated with this hydrocarbon oil to assess if the sample could be cleaned up, regardless of which fraction the TCDF standard was eluting. Overall, the sample was slightly cleaned up. However, it was not enough to warrant processing the full sample and injecting onto the GC. Because of this issue, the last 5 samples could not be tested for TCDD/F detection.

There are many speculations to the source of this hydrocarbon oil as three of the five samples were from the same core, and at depths that surrounded the 10-12cm depth (6-8cm, 14-16cm, and 20-22cm) in which TCDD was detected. This could indicate that the oil was a contamination added somewhere during the processing of the sample and not necessarily part of the sediment itself. A possible source of contamination is contact with plastics, which were frequently used with caps for vials, components in the ASE machine itself, and other lab equipment.

An observation was made during the processing of these 5 samples that was not noticed during the processing of the samples that showed no signs of oil, and could indicate the source of the oil was from the sediment. While emptying the ASE cells after the extraction, it was observed that portions of the ASE cell that contained sulfuric acid activated silica gel turned a distinct yellow color, as opposed to the previously observed white color (Fig. 9). This could mean that these specific samples possibly had higher lipid contents than previous samples, and overloaded the silica gels ability to retain hydrocarbons, which then leaked into the sample. Alternatively, the sulfuric acid activated silica gel could have become too deactivated through the absorption of water, despite being stored in a desiccator, which could

also affect its ability to retain hydrocarbons. Overall the method has potential for future use in assessing sediments for TCDD/F as an alternative to high cost of testing using EPA standard methods.



Figure 9. Emptied contents of an extracted ASE cell. Starting from the top (left) is the sediment, GF/F filter, sulfuric acid activated silica gel, GF/F filter, neutral silica gel, and a last GF/F filter. The yellow portion of the sulfuric acid activated silica gel was not seen before samples started containing hydrocarbon oil.

Conclusion

The 7.79mm year^{-1} sedimentation rate observed in Muchalat is conducive for studying TCDD/F concentrations, as a box core will easily capture sediment from the 28 year period in which the pulp mill was operational. Since regulations have prohibited the release of dioxins and furans in mill effluent since 1992, and the eventual closing of the mill in 1998, alarming concentrations of TCDD have persisted within the sediment. Because the sediment core appears largely undisturbed, it is unlikely that these concentrations could make it to the surface and circulated throughout the food chain. However, this does not mean they are fully sequestered.

The one-step extraction process is effective at removing TCDD/F from sediment, but may require additional cleanup steps, especially for sediments likely to contain sulfur. Additionally, because the source of the hydrocarbon contamination can only be speculated, it is possible that this method will not work entirely unless a method for removing the oil and retaining the TCDD/F concentrations can be found. Further investigation into the extent of TCDD/F contamination in sediment from the Gold River pulp is needed for a better understanding into how these bleach kraft operations affect the surrounding environments long after they close.

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